REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1 7 1990

AD-A226 646

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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 8/6/90	3. REPORT TYPE AND DATES COVERED Final 7/1/88 – 11/30/89

4. TITLE AND SUBTITLE
PBT-PBO-Based Hybrid Polymers with Nonlinear Optical Properties or High Electrical Conductivity

5. FUNDING NUMBERS
F49620 88-C-0122

6. AUTHOR(S)
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61102F 2303 A3
AFOSR-88-C-1022

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

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AFOSR-TR· 90 1025

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

AFOSR/NC
Building 410, Bolling AFB DC
20332-6448

DTIC
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SEP 19 1990
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10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

This program has involved a combined synthetic, processing, and physicochemical study of multifunctional, high-performance polymer systems rationally designed for certain unusual physical properties. In one thrust, the unique properties of the high modules/high strength macromolecules poly(p-phenylenebenzabisthiazole) (PBT) and poly(p-phenylenebisoxazolo) (PBO) have been utilized to develop new kinds of electrically conductive polymeric and molecular/macromolecular hybrid materials. In the second thrust, several complementary approaches to the construction, evaluation, and fundamental understanding of new types of high-performance nonlinear optical materials have been pursued. Areas of emphasis have included chromophore-functionalized glassy polymers, chromophore-embedded crosslinkable matrices, inorganic/organic hybrid materials, crosslinked NLO films, the design of novel chromophores, and internally ordered polymeric NLO materials. Each research component has built upon past successes as well as upon strong on-going collaborations in laser optics and quantum theory.

14. SUBJECT TERMS
Polymer, Nonlinear optics, Chromophore, Second harmonic generation

15. NUMBER OF PAGES
22

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18

COMPLETED PROJECT SUMMARY

TITLE: PBT, PBO-Based Hybrid Polymers with Nonlinear Optical Properties

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INCLUSIVE DATES: July 1, 1988 - November 30, 1989

CONTRACT/GRANT NUMBER: AFOSR-F49620-88-C-0122

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PUBLICATIONS:

1. Rational Construction of Polymeric Nonlinear Optical Materials. Properties of Chromophore-Functionalized Polystyrenes, C. Ye, N. Minami, T. J. Marks, J. Yang, and G. K. Wong, Mats. Res. Soc. Proc., 109, 263 (1988).

2. Nonlinear Optical Materials Based on Benzobisthiazole. Electronic Structure/Molecular Architecture/Polarizability/Hyperpolarizability Relationships Derived from π-Electron Theory, Dequan Li, T. J. Marks, and M. A. Ratner, Mats. Res. Soc. Proc., 109, 149 (1988).

3. Conductive Polymers Based Upon Rigid-Rod Ultra-High-Modulus Macromolecules. Electrochemical Doping of Poly(p-phenylenebenzobisthiazole) (PBT), P. A. DePra, J. G. Gaudiello, and T. J. Marks, Macromolecules, 21, 2215 (1988).

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5. Synthetic Approaches to Stable and Efficient Polymeric Frequency Doubling Materials. Second-Order Nonlinear Optical Properties of Poled, Chromophore-Functionalized Glassy Polymers, C. Ye, N. Minami, and T. J. Marks, J. Yang, and G. K. Wong, in "Nonlinear Optical Effects in Organic Polymers," J. Messier, F. Kajzar, P. N. Prasad, and D. R. Ulrich, eds., Kluwer

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10. Electrically Conductive Molecular Composites Based Upon PPBT and Metallophthalocyanines: Processing, Microstructure, and Electrochemistry, P. A. DePra, J. M. Giesler, T. J. Marks, and S. H. Carr, Mats. Res. Soc. Proc., 134, 673 (1989).

11. Polyphenylene Ether-Based Thin Film Nonlinear Optical Materials Having High Chromophore Densities and Alignment Stability, D. Dai, T. J. Marks, J. Yang, and G. K. Wong, Macromolecules, in press.

12. Chromophore-Functionalized Polymeric Thin Film Nonlinear Optical Materials. Effects of In Situ Cross-linking on SHG Temporal Characteristics, J. Park, T. J. Marks, J. Yang, and G. K. Wong, submitted for publication.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This program has involved a combined synthetic, processing, and physicochemical study of multifunctional, high-performance polymer systems rationally designed for certain unusual physical properties. In one thrust, the unique properties of the high modules/high strength macromolecules poly(p_-phenylenebenzabisthiazole) (PBT) and poly(p_-phenylenebisoxazolo) (PBO) have been utilized to develop new kinds of electrically conductive polymeric and molecular/macromolecular hybrid materials. In the second, larger thrust, several complementary approaches to the construction, evaluation, and fundamental understanding of new types of high-performance nonlinear optical materials have been pursued. Areas of emphasis have included chromophore-functionalized glassy polymers, chromophore-embedded crosslinkable matrices, inorganic/organic hybrid materials, crosslinked NLO films, the design of novel chromophores, and internally ordered polymeric NLO materials. Each research component has built upon past successes as well as upon strong on-going collaborations in laser optics and quantum theory.

Polymeric materials offer unique diversity and tailorability with respect to strength, flexibility, light weight, environmental stability, toughness, and amenability to processing into films, foils, coatings, fibers, etc. Until recently, the application of polymers in optics technology has been limited largely to inexpensive lenses, prisms, fiber optics, filters, and coatings. This picture, however, has dramatically changed, and the recent advent of organic materials having unusual and impressive nonlinear optical (NLO) characteristics signals that new generations of materials for optics and optoelectronics technology await synthesis, characterization, understanding, and ultimate application. The attraction of NLO materials based on organic π-electron chromophores vis-á-vis the more traditional inorganic substances (e.g., KDP, KTP, $LiNbO_3$)[2] lies in the possibility of large nonresonant susceptibilities, ultrafast response times, low dielectric constants, high damage thresholds, and the inherent tailorability of organic molecules.[1] Polymeric organic NLO systems offer, in addition, the possibility of high mechanical and environmental stability, supermolecular structural organization, low cost, and ready process- ability into films, fibers, waveguides, etc.

The fundamental relationship describing the change in molecular dipole moment (polarization) upon interaction with an oscillating external electric field can be expressed in a power series (eq.(1)).[1,2] Here P_i is the

$$P_i = \sum_j \alpha_{ij} E_j + \sum_{jk} \beta_{ijk} E_j E_k + \sum_{jkl} \gamma_{ijkl} E_j E_k E_l + \cdots \qquad (1)$$

polarization induced along the ith molecular axis, E_j is the jth component of the applied electric field, α is the linear polarizability, β the quadratic hyperpolarizability, and γ the cubic hyperpolarizability. The even order tensor,

β, which is responsible for second harmonic generation (SHG) and other first-order NLO effects, vanishes in a centrosymmetric environment. There are no environmental parity restrictions on the odd order tensors. The analogous macroscopic polarization arising from an array of molecules (e.g., in a crystal) is given by eq.(2) where the χ's are macroscopic susceptibilities, and indices

$$P_I = \sum_J \chi_{IJ}^{(1)} E_J + \sum_{JK} \chi_{IJK}^{(2)} E_J E_K + \sum_{JKL} \chi_{IJKL}^{(3)} E_J E_K E_L + \cdots \qquad (2)$$

refer to crystallographic directions. The macroscopic susceptibilities are related to the corresponding molecular terms α, β, γ, etc. by local field corrections (arising from intermolecular interactions) and the density of chromophores as in eq.(3) for frequency-doubling. Here N is the number of

$$\chi_{IJK}^{2\omega}(-2\omega;\omega,\omega) = N \, f_{Ii} \, f_{Jj} \, f_{Kk} \, \beta_{ijk}(-2\omega;\omega,\omega) \qquad (3)$$

molecules per unit volume and the f's are local field corrections. Importantly, it can be seen that the nonlinear response of a material is ultimately governed both by the optical characteristics of constituent molecular chromophores and by the overall spatial organization (e.g., noncentrosymmetry for $\chi^{(2)}$) that can be imposed upon large ensembles of these constituents. The great scientific challenge here lies in devising new and more effective approaches to the synthesis and processing of polymeric NLO systems for ever higher performance characteristics as well as in developing deeper fundamental understandings of organizational and dynamic processes within polymer films, of interfaces between polymers and other surfaces, and of the electronic structural aspects of how single molecules and molecular ensembles interact with electromagnetic radiation.

It is our conviction that major research progress in the area of new nonlinear optical materials requires an integrated, multidisciplinary attack

involving closely coupled synthesis, processing, physical characterization, and theory. The present report describes the continuation of just such an effort, focused primarily on testing new ideas about polymeric $\chi^{(2)}$ and $\chi^{(3)}$ materials. Interfaced activities at Northwestern which are closely integrated with this effort have included a theoretical initiative (Professor Mark Ratner), and high-level laser characterization (Professor George Wong).

The primary research activities to date have addressed the challenge of how best to incorporate optimum $\chi^{(2)}$ and $\chi^{(3)}$ NLO characteristics into selected polymeric systems and how, for $\chi^{(2)}$ materials, to effectively construct and stabilize necessarily noncentrosymmetric microstructures. Several research thrusts are in progress (vide infra) and major advances have been achieved. In addition to polymer work, efforts aimed specifically at inorganic/organic hybrid materials, organized thin NLO films, and the design of new chromophores have been initiated. Although our efforts have not been specifically directed toward device fabrication and development, we are aware of the recent exciting advances in this area[3] and are anxious to "spin-off" certain of our materials at the appropriate stage of the synthesis/characterization sequence. As preludes to such "spin-off" transitions, initial waveguide fabrication and characterization studies have been carried out at Northwestern. In the narrative which follows, we discuss, by area, our progress to date over the relevant contract period.

I. NLO Chromophore-Functionalized Glassy Polymers

Covalently linking selected NLO chromophores to the backbones of high-T_g,T_β glassy polymers with well-characterized molecular weight properties followed by poling in an electric field offers an extremely attractive approach to the fabrication of polymeric frequency doubling materials.[2b,4,5] Without

poling, these polymers offer an equally attractive approach to frequency tripling materials. In comparison to simply doping "host" polymers with NLO guests,[6,7] the present strategy offers the possibility of very high chromophore densities (phase separation should be impeded), high chemical and thermal integrity (the chromophores are locked into the matrix), temporal stability of field-induced chromophore noncentrosymmetric alignment (slowing of chromophore reorientation as a consequence of attachment to the backbone), and tailorability (a great many chromophore/backbone combinations are possible).

The excellent transparency, relatively high T_g/T_β, low dielectric constant, good film-forming characteristics, and amenability to chemical functionalization of polystyrene motivated our investigations of chromophore-functionalized polystyrene (PS) systems I,II (synthesized from $(\underline{p}\text{-}(PS)CH_2I)^{4a,b}$ and III (from $(p\text{-}PS)OH)^{4c\text{-}g}$ prepared at varying levels of chromophore incorporation. System II offers a salt-like structure, which may retard chromophore motion (raise T_g, reduce free volume), while unfunctionalized OH groups of III provide a structure-enforcing hydrogen-bond network[8] (again, raise T_g,T_β and reduce free volume). The chromophores employed to date were chosen to test various ideas and are by no means the highest β chromophores available. Thus, R is a common dye molecule, R' offers a salt-like microstructure which should have a very high T_g,T_β, and R" is chiral, ensuring noncentrosymmetry even in cases of extensive chromophore aggregation.
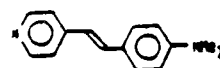
Results to date are very encouraging and warrant detailed studies of SHG and THG characteristics as a function of key synthetic and processing parameters, as well as careful evaluation of current poling/performance models. Initial experiments indicate that polymers I, II, and III can be prepared at monomer
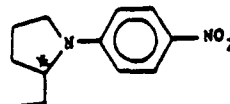
$R = DR1 =$
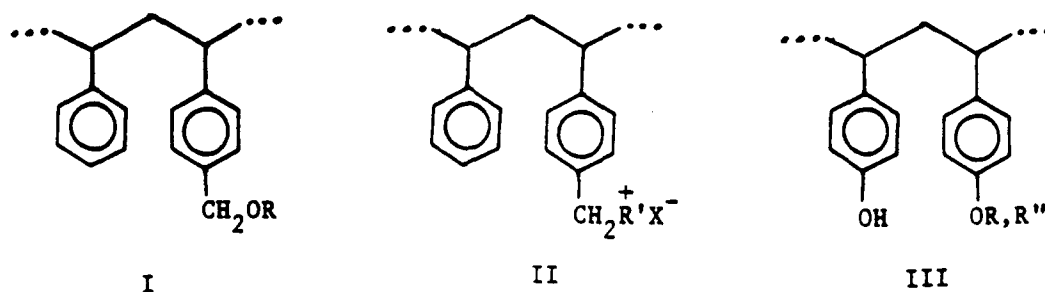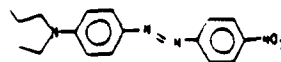
$R' = DASP =$

$R'' = NPP =$

unit functionalization levels as high as ca. 60% and that such materials form films with excellent transparency and mechanical properties. With careful fabrication methodology, it is possible to pole these films at fields as high as 1.8 MV/cm. In contrast, attempts to prepare films in which polystyrene or (PS)OH is doped with the same NLO chromophores result in phase separation at rather low chromophore concentrations (ca. 5 mol%), films with poor transparency, and films that frequently undergo dielectric breakdown (presumably a consequence of the enhanced molecular mobility).

We find that annealing has a significant effect on film properties, in that the ultimate poling fields which can be employed are increased and the temporal stability of SHG efficiency is enhanced. The cause appears to be removal of traces of solvent and other volatiles (verified by FT-IR data) which plasticize

the matrix and enhance macromolecule mobility (supported by DSC data), independent or concurrent changes in the hydrogen bonding network in the case of (PS)OH-based materials (verified by FT-IR data) which is also likely to affect mobility, and changes in film morphology (suggested by SEM data) which may seal imperfections leading to dielectric breakdown during poling.

Film second harmonic coefficients at 532 nm were calculated from the angular dependence of the SHG intensity and the standard treatment for uniaxial materials, assuming also that $d_{31} = d_{24} = d_{15} = 1/3 \ d_{33}$.[9] Coefficients for (PS)O-DR films are uncorrected for absorption effects and should be regarded as underestimations. As can be seen in Table I, the second harmonic coefficients are generally rather large, exceeding the corresponding d_{36} of KDP (1.1 x 10^{-9} esu) and frequently equalling or exceeding d_{31} of LiNbO$_3$ (14.2 x 10^{-9} esu).

A simple isolated molecule, Langevin description of chromophore behavior in an electric field predicts the relationship shown in eqs.(4) and (5).[6a-c]

$$d_{33} = \frac{1}{2} \ Nf^{2\omega}f^{\omega}f^{\omega} \ \beta_{zzz} \ L_3(p) \tag{4}$$

$$p = \frac{f^o\mu E_p}{kT} \tag{5}$$

Here N is the chromophore number density, μ is the chromophore molecular dipole moment, β_{zzz} is the appropriate molecular hyperpolarizability tensor, E_p is the poling field, L_3 is the third order Langevin function, and the f's are the corresponding local field factors. For the (PS)O-NPP systems, preliminary indications are that d_{33} is approximately proportional to N as predicted by this model. We also find that d_{33} is approximately proportional to E_p for fields below ca. 0.6 MV/cm. However, there is a departure from linear behavior (saturation) at the highest fields. Indeed, the model predicts such saturation effects when $f^o\mu E_p$

$\approx$ kT, which we estimate to be when $E_p \geq 1.3$ MV/cm for (PS)O-NPP. Table I illustrates the generally favorable agreement between experimental d_{33}

Table I. Second Harmonic Coefficients for Chromophore-Functionalized Poly(p-Hydroxystyrenes).[a]

Polymer	Functionalization Level (% Phenyl Rings)	Poling Field (MV/cm)	τ_2 (days)[b]	$(10^{-9} d_{33}$ esu)[c]
(PS)CH$_2$-Dr	13	0.3		2.7
(PS)CH$_2$-DASP	5	0.3		0.12
(PS)CH$_2$-NPP	36	0.7		3.8(8.9)
(PS)O-DR	11	1.8	38	10.6
(PS)O-DR[d]	14	1.1	109	3.1
(PS)O-DR	50	1.1	37	16.7
(PS)O-NPP	15	0.7	313	5.1(5.7)
(PS)O-NPP	25	0.3	195	3.0(3.6)
(PS)O-NPP	48	0.6		11.6(10.9)
(PS)O-NPP	48	1.6	42	18.0(29)

[a]Measured within 0.5 h of poling; $\lambda = 1064$ nm.
[b]Long-term SHG decay lifetime from fitting to eq.(6).
[c]Experimental SHG coefficients. Theoretical values calculated from eq.(4) are given in parentheses.
[d]Prepared from $M_W = 98,000$ (PS)OH; all other samples from $\overline{M}_W = 6,000$ (PS)OH.

values and those estimated from eqs.(4) and (5) using the published $\mu\beta_{zzz}$ value for NPPOH[10] and optical constants for polystyrene. There are deviations, however, which suggest that the generality of this model must be further scrutinized.

The temporal stability of SHG efficiency reflects complex reorientational processes by which the field-induced chromophore orientations relax to thermodynamic equilibrium/minimum free volume.[11] Unlike the doped chromophore/ polymer systems studied to date, the persistence of functionalized polymer SHG is generally long-lived. The restricted chromophore mobility imparted by

covalent linkage to the polymer backbone as well as by hydrogen-bonding networks are doubtless important factors. Typical (PS)O-NPP d_{33} decay data at room temperature (25±3°C) are shown in Figure 1. The effects of film annealing are clearly evident and are in accord with the other changes in film properties noted above. Figure 2 shows d_{33} decay data for an annealed (PS)O-DR film. It is found that the d_{33} decay curves for all the (PS)O-R films cannot be fit to a single exponential, suggesting that several relaxation processes are operative. Fits to a two-exponential model (eq.(6)) are more convincing, and derived long-

$$d_{33} = Ae^{-t/\tau_1} + Be^{-t/\tau_2} \qquad (6)$$

term decay lifetimes are compiled in Table I. We find that the amplitude of the
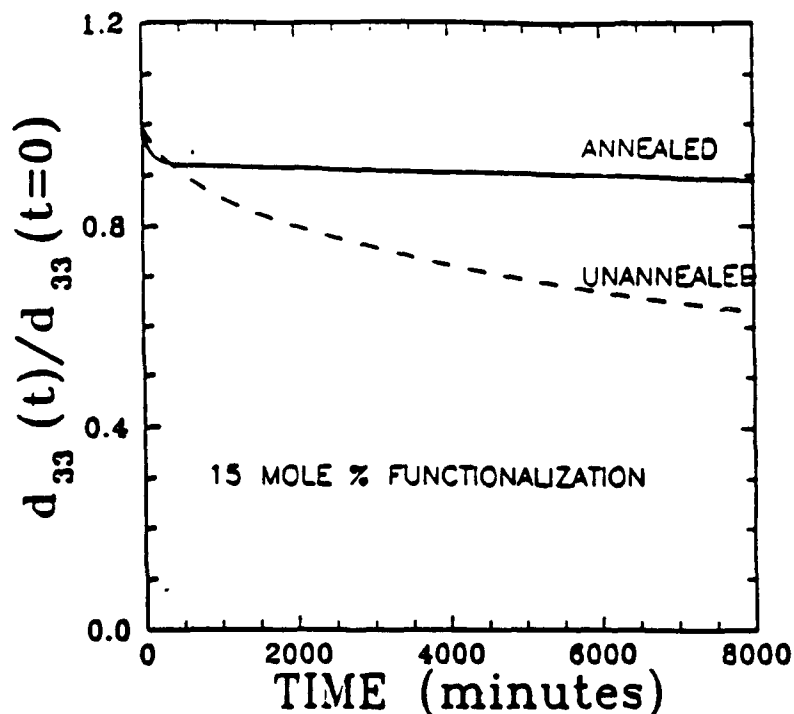

Figure 1. Temporal characteristics of the second harmonic coefficient of a (PS)O-NPP film ((PS)OH, $M_W = 6,000$; 15% functionalization level) showing the effects of film annealing. The poling field was 0.7 MV/cm.

short-term process is more sensitive to the presence of THF and can be diminished by annealing. This observation suggests that the short-term process involves facile chromophore reorientation in THF-rich (high local free volume) microenvironments. Preliminary experiments also indicate that the long term decay rate of d_{33} is decreased at higher polymer molecular weights and increased at higher chromophore densities and at higher poling fields. Clearly, these patterns must be substantiated and understood by additional experiments.

For all of the (PS)O-R polymers, it is noteworthy that successful poling can be carried out at temperatures substantially below T_g (which is ca. 100-110°C). In situ experiments are being conducted in which SHG characteristics are monitored during the poling process. As can be seen from the preliminary data in Figure 3, preferential chromophore orientation can be induced at
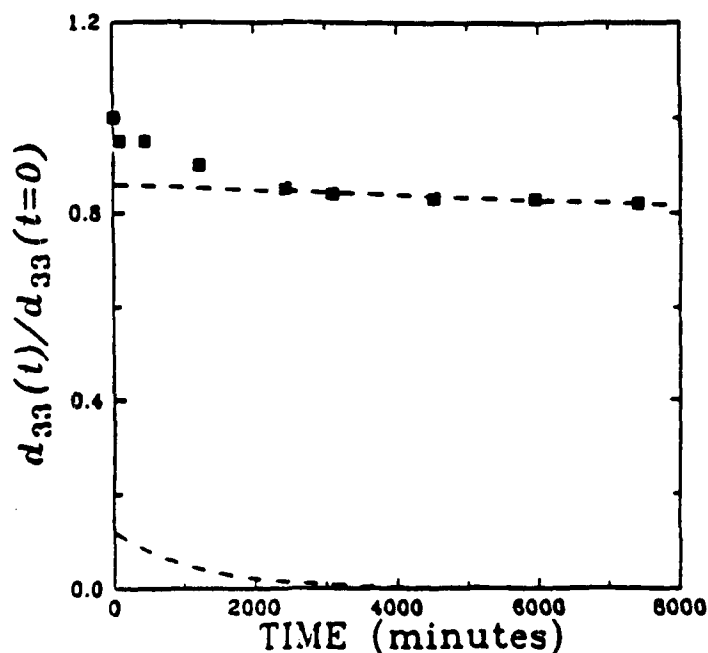

Figure 2. Temporal characteristics of the second harmonic coefficient of an annealed (PS)O-DR film ((PS)OH, M_w = 98,000; 14% functionalization level) poled at 1.05 MV/cm. The dashed lines show the two-component fit to eq.(6).

temperatures considerably below T_g, with the rate of approach to asymptotic behavior being a strong function of temperature. Also noteworthy is the rather abrupt decline in SHG signal with removal of the poling field and how this decline depends upon temperature. These results suggest the presence within the polymer of substantial, poling-induced free volume at the point of poling field termination. Further _in situ_ studies of these phenomena should be extremely informative.
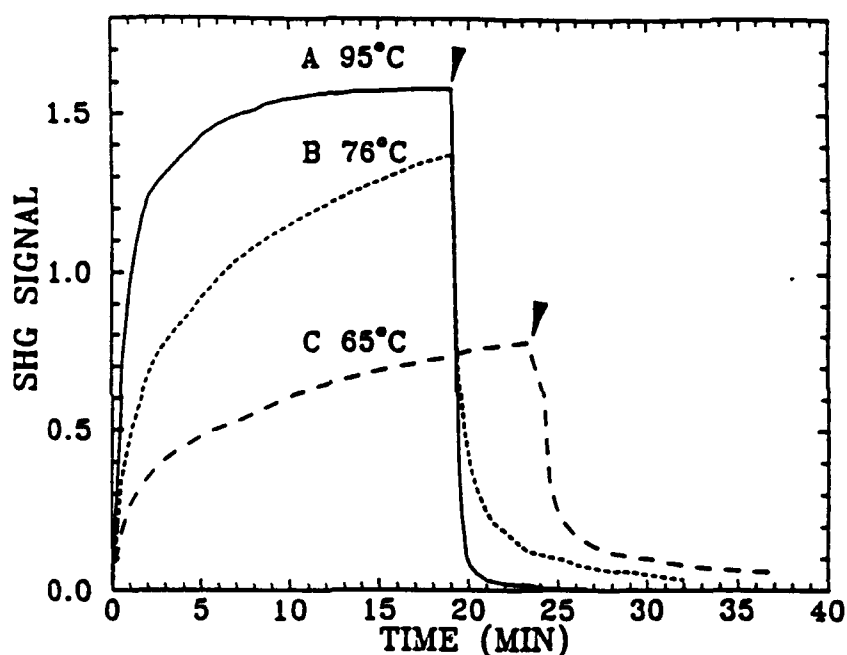

Figure 3. _In situ_ study of SHG response as a function of poling conditions for a (PS)O-NPP film (48% functionalization level). The poling field is 0.375 MV/cm. The arrows indicate the point at which the poling field is removed.

II. Chromophore-Embedded Crosslinkable Matrices

Another attractive strategy for producing polymeric NLO materials with immobile chromophores would be to disperse high-β or high-γ guest chromophores in an optically transparent host matrix which could then be simultaneously poled and chemically crosslinked (eq.(7)).[12] In preliminary investigations,

solutions of high-β chromophores **VI** and **VII** were prepared in uncured optical-

$$\xrightarrow[\text{cross-link}]{\mathcal{E}_p} \tag{7}$$
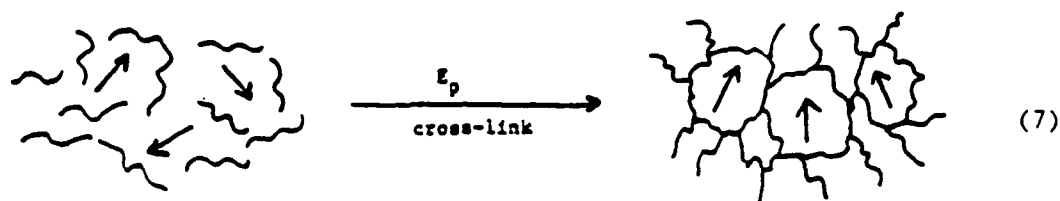
grade epoxy matrices and sandwiched between ITO glass plates. The matrix could

then be cured by heating at 80°C for varying times. Parallel experiments between

NaCl plates established curing rates by infrared spectroscopy. It was found in

$(CH_3)_2N$—⬡—$CH{=}CH$—⬡—NO_2 $(C_6H_5)(H)N$—⬡—$N{=}N$—⬡—NO_2

VI   **VII**
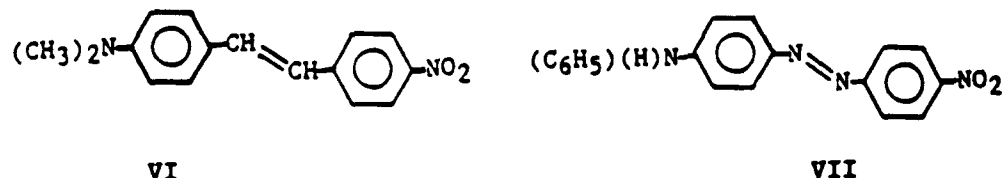
preliminary experiments that the uncured matrices readily underwent dielectric

breakdown when poling was attempted. Thus, partial curing for 0.75-1.2 h at 80°C

was necessary before poling fields could be applied. Fields up to 0.6 MV/cm were

then gradually applied and curing continued at 80°C. Optical characterization

of the resulting epoxy films included both measurements of the coherence lengths

by the wedge technique (typically ca. 10 μm) and SHG measurements. Samples not

doped with chromophores, unpoled, or cured for short times exhibit no SHG signal.

The latter observation is consistent with rapid chromophore reorientation in the

partially cured matrix (_vide infra_). Preliminary studies of d_{33} parameters

reveal trends in good agreement with eqs.(4) and (5). Magnitudes are, however,

limited by the solubilities of these particular chromophores.

The temporal characteristics of d_{33} are illustrated for typical poled,

crosslinked chromophore/epoxy matrices over short and long time periods in Figure
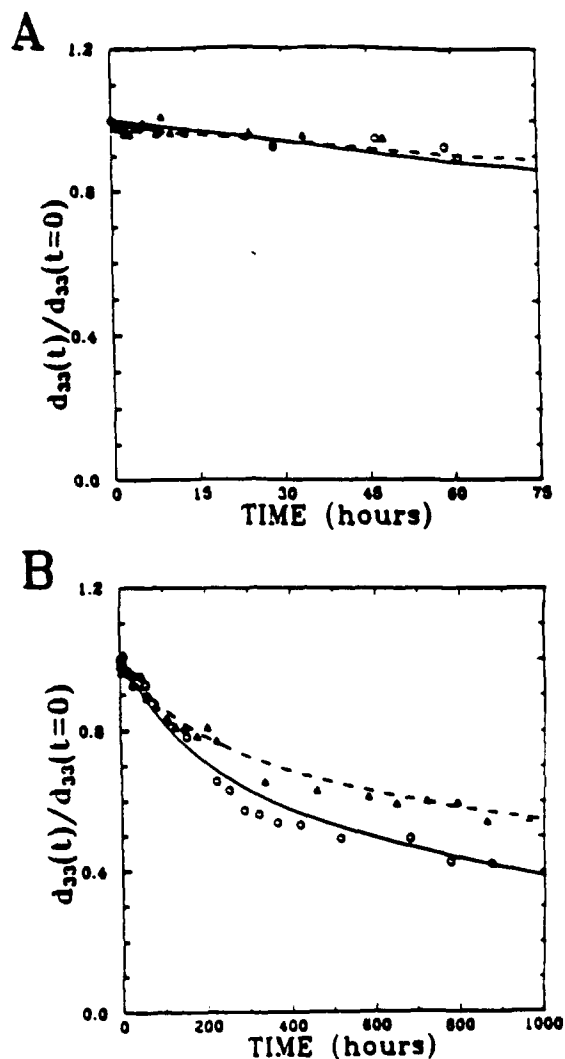
Figure 4. Temporal characteristics at room temperature of the second harmonic coefficient d_{33} for poled NLO chromophore-epoxy films containing chromophore VIII (o) or chromophore IX (Δ). A. Short-term decay. B. Long-term decay. Solid lines are the numerical fit to eq.(6).

4. Most striking is the enhancement in overall SHG temporal stability compared to non-crosslinked guest-host systems.[6,7] As in the case of chromophore-functionalized polymers,[4] the decay data could not be fit to a single exponential.

More satisfactory numerical fits to a double exponential (eq.(6)) are also shown in Figure 4. As suggested earlier, such bimodal behavior is plausibly associated with disparate chromophore reorientation rates in regions of free volume above and below a certain critical free volume threshold.[12,13] Derived fitting parameters for the $d_{33}(t)$ data shown are $\tau_1 = 7$, $\tau_2 = 72$ days for the VI-containing matrix and $\tau_1 = 8$, $\tau_2 = 142$ days for the VII-containing matrix. A correlation between decay time and chromophore dimensions has been noted previously[7b] and, in the present case, likely reflects the diminished mobility of the more massive DO1 chromophore molecule.

Further insight into the response of chromophore mobility to the matrix crosslinking/densification process is provided by *in situ* measurements of the SHG signal intensity as a function of temperature, poling field, and matrix curing time. In these experiments, film samples were subjected to repeated cycles of curing in a poling field, cooling to room temperature, and removal of the poling field. Although detailed numerical analyses of the data are still in progress, two effects are immediately evident in the data (Figure 5). As anticipated from the Boltzmann-like form of eqs.(4) and (5), decreasing the sample temperature from 360 → 300 K is accompanied by a corresponding increase (ca. 40% is predicted) in $I^{2\omega}$. While such behavior is not unexpected in more fluid examples (e.g., Figures 5a,b), the relatively rapid response at higher crosslinking levels (Figures 5c,d) indicates significant residual orientational mobility (at least over relatively small angular excursions and at 88°C -- *vide infra*). For lightly crosslinked samples, removal of the poling field results in a precipitous drop in $I^{2\omega}$, followed by a levelling-off (Figures 5a,b). As the matrix crosslinking process progresses, the magnitude of the room temperature zero-field decline steadily decreases, and $I^{2\omega}$ at the levelling-off point

correspondingly increases. An attractive tentative explanation for this behavior invokes a decreasing component of the free volume distribution greater than the critical threshold for chromophore reorientation as the degree of matrix cross-
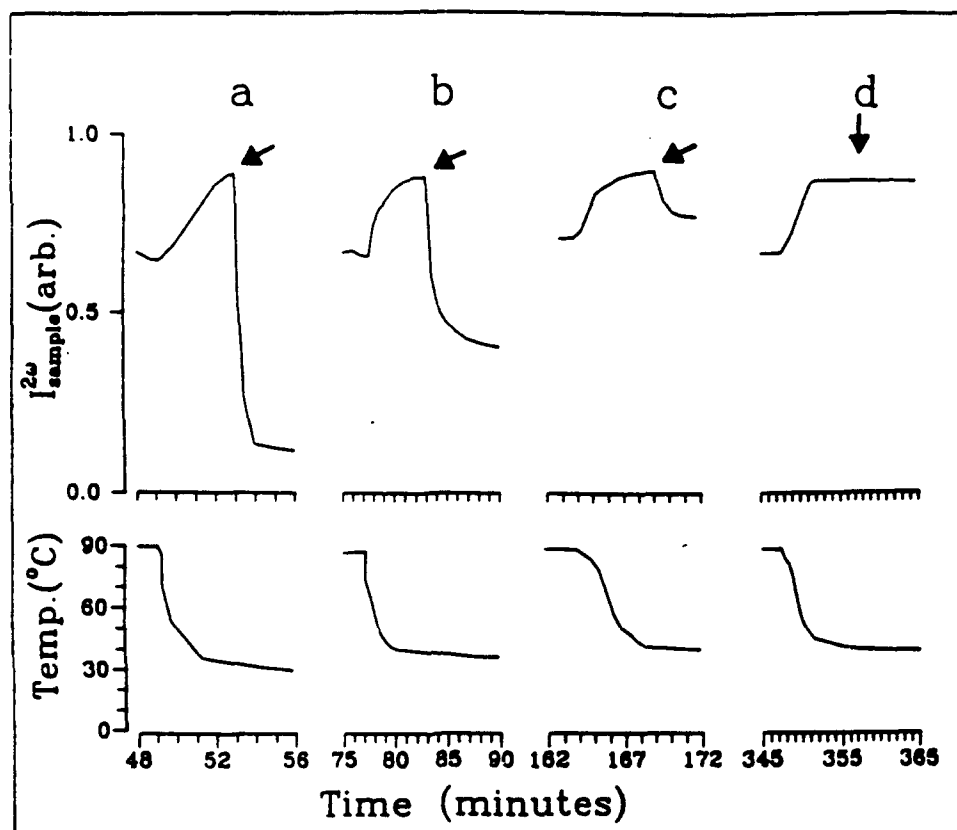

Figure 5. Response of the 532 nm second harmonic signal intensity $I^{2\omega}$ of chromophore IX-epoxy film to curing time, temperature, and electric poling field. The time ordinate gives total accumulated curing time while the arrows indicate the time of removal of the 4.8×10^5 V/cm poling field. Not shown: The temperature was returned to 88°C and the poling field reapplied after each experimental sequence.

linking increases. That $I^{2\omega}$ in Figure 5d responds rapidly to the temperature drop but not to the removal of the poling field can be explained by the closer temperature proximity of the former process to the matrix T_g.

III. Inorganic/Organic Hybrid NLO Materials

Numerous classes of chemical transformations are now known in which organic molecules can be inserted ("intercalated") into the van der Waals gaps of layered inorganic solids (eq.(8)).[13] In most cases, the geometry of the host layer

(8)
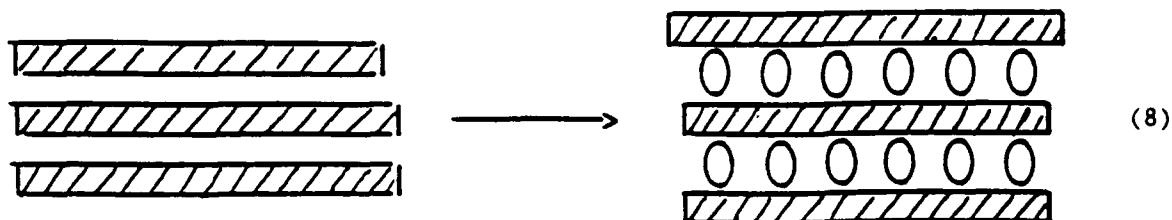
structure largely dictates the resulting orientation of the guest molecules. In regard to the construction of NLO materials, the intercalation of high-β NLO chromophores into the crystal structures of acentric layered materials suggests a new route to crystalline inorganic/organic hybrid structures with highly oriented chromophore assemblies. Our initial studies[14] have focused on optically transparent mica-like kaolinite and dickite materials in which aluminosilicate layers form acentric ABCABCABC patterns.[15,16] Such materials undergo intercalation reactions, and guest molecules can be oriented by networks of hydrogen bonds (e.g., the single crystal diffraction results in Figure 6).

We find by powder X-ray diffraction and elemental analysis that kaolinite undergoes intercalation by pyridine-N-oxide chromophores (VIII) to yield yellow

$R = H, NH_2, NMe_2, NO_2$
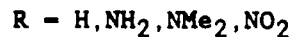
VIII
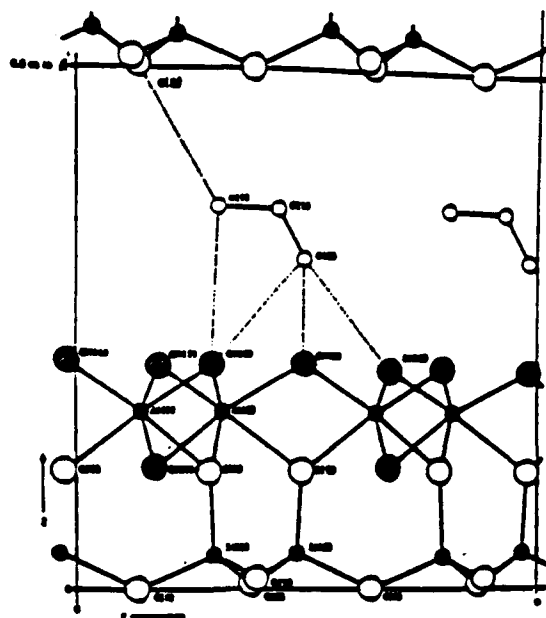
Figure 6. Projection of the structure of the dickite-formamide intercalate perpendicular to the layer planes. Single crystal diffraction results from ref. 15.

or orange powders.[14] Preliminary powder SHG experiments reveal significant $I^{2\omega}$ signals that are not discharged by extensive sample washing[17] (i.e., which are not likely due simply to chromophore adsorption on the surface).

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COMPLETED PROJECT SUMMARY

TITLE: PBT, PBO-Based Hybrid Polymers with Nonlinear Optical Properties
         or High Electric Conductivity

PRINCIPAL INVESTIGATORS:
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INCLUSIVE DATES: July 1, 1988 - November 30, 1989

CONTRACT/GRANT NUMBER: AFOSR-88-C-1022

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ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This program has involved a combined synthetic, processing, and physico-
chemical study of multifunctional, high-performance polymer systems rationally
designed for certain unusual physical properties. In one thrust, the unique
properties of the high modules/high strength macromolecules poly(p-phenylene-
benzabisthiazole) (PBT) and poly(p-phenylenebisoxazolo) (PBO) have been utilized
to develop new kinds of electrically conductive polymeric and molecular/macro-
molecular hybrid materials. In the second, larger thrust, several complementary
approaches to the construction, evaluation, and fundamental understanding of new
types of high-performance nonlinear optical materials have been pursued. Areas
of emphasis have included chromophore-functionalized glassy polymers, chromo-
phore-embedded crosslinkable matrices, inorganic/organic hybrid materials,
crosslinked NLO films, the design of novel chromophores, and internally ordered
polymeric NLO materials. Each research component has built upon past successes
as well as upon strong on-going collaborations in laser optics and quantum
theory.